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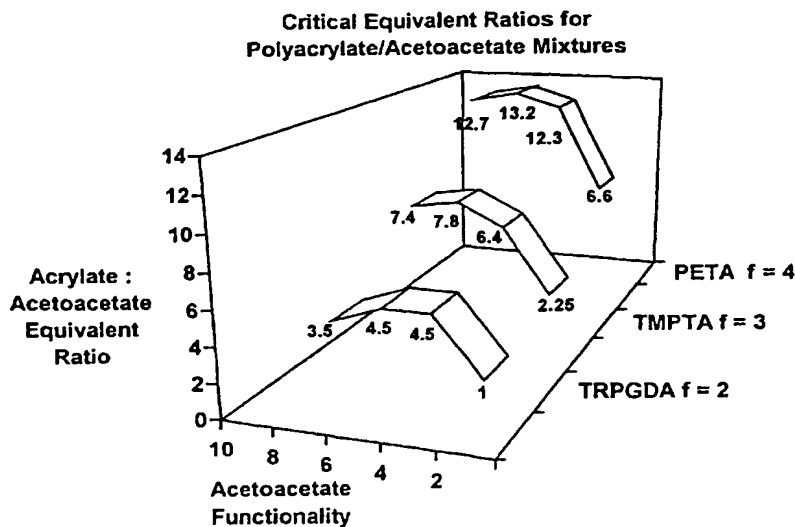
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(54) Title: LIQUID OLIGOMERS CONTAINING UNSATURATION



(57) Abstract: The liquid oligomeric compositions of this invention are made by the Michael addition reaction of acetoacetate functional donor compounds with multifunctional acrylate receptor compounds where the equivalent ratios of multifunctional acrylate to acetoacetate vary from  $\geq 1 : 1$  to  $\geq 13.2 : 1$  depending on the functionality of both multifunctional acrylate and acetoacetate. Unusable gelled or solid oligomer products occur below the claimed ranges. The oligomers of this invention are further crosslinked to make coatings, laminates and adhesives.

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## LIQUID OLIGOMERS CONTAINING UNSATURATION

## FIELD OF THE INVENTION

5           This invention relates to liquid oligomers containing unsaturation which can be crosslinked using ultraviolet light without adding costly photoinitiators. Films made from the crosslinked oligomers of the inventions are used as protective or decorative coatings on various substrates. The oligomers can be added to other resins used in adhesives or composites.

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## BACKGROUND OF THE INVENTION

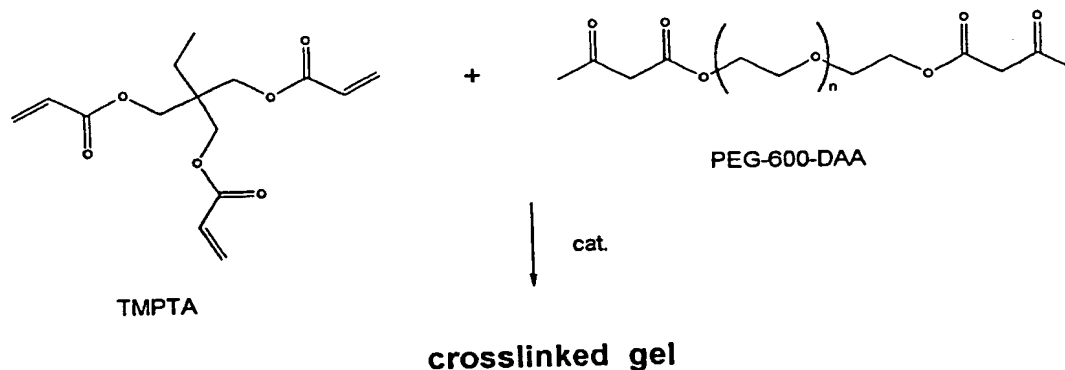
          Acrylate, methacrylate and other unsaturated monomers are widely used in coatings, adhesives, sealants, and elastomers, and may be crosslinked by ultraviolet light radiation or peroxide initiated free radical cure.

15   These are typically low molecular weight multifunctional compounds which may be volatile or readily absorbed through skin and can cause adverse health effects. Functionalized polymers may overcome some of these drawbacks; generally, polymers are nonvolatile compounds, not readily absorbed through skin. However, multistep syntheses may be required, low

20   functionality may be detrimental to reactivity and final properties, and catalyst or initiator may be required to effect crosslinking.

          The Michael addition of acetoacetate donor compounds to multiacrylate receptor compounds to make crosslinked polymers has been

described in the literature. For example, Mozner and Rheinberger reported the Michael addition of acetoacetates having a  $\beta$ -dicarbonyl group to triacrylates and tetracrylates. Macromolecular Rapid Communications 16, 135-138 (1995). The products formed were crosslinked gels. In one of the reactions, Mozner added one mole of trimethylol propane triacrylate (TMPTA) having 3 functional groups to one mole of polyethylene glycol (600 molecular weight) diacetoacetate (PEG-600-DAA) having two functional groups. (Each "acetoacetate functional group" reacts twice, thus each mole of diacetoacetate has four reactive equivalents.)



Mole Ratio of TMPTA : PEG 600 DAA = 1 : 1

Ratio of acrylate : acetoacetate functional groups = 3 : 2

Ratio of reactive equivalents = 3 : 4

10

## BROAD DESCRIPTION OF THE INVENTION

This invention is the discovery that certain soluble liquid uncrosslinked oligomers, made by one step Michael addition of acetoacetates to multi-

acrylates, can be further crosslinked using ultraviolet light without using costly photoinitiators.

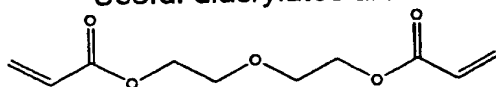
We have discovered that when precise proportions of multiacrylate acceptor compounds to acetoacetate donor compounds are combined using a basic catalyst, liquid oligomeric compositions are the product. If proportions below the claimed ranges are used, crosslinked gels or solid products are made which are not useful for the purposes of this invention because only un-gelled, uncrosslinked liquid oligomers will further crosslink without adding photoinitiators. In addition, the liquid oligomer compositions of this invention, since they are liquids, can readily be applied to various substrates using conventional coating techniques such as roll or spray prior to ultraviolet light cure.

The graph illustrates that ratios below the three curves were unuseable gelled materials outside the scope of the invention. Ratios on or above the curves are the liquid oligomers of this invention.

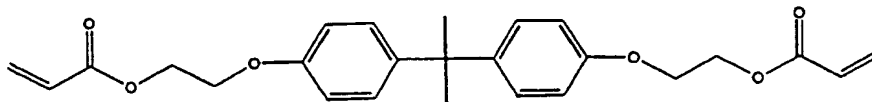
#### DETAILED DESCRIPTION OF THE INVENTION

Among the multiacrylates used to make the oligomers of this invention are diacrylates, triacrylates, and tetraacrylates.

Useful diacrylates are:

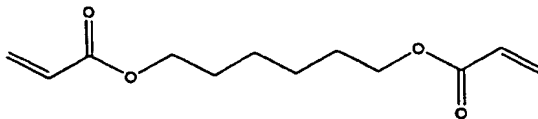


Diethylene Glycol Diacrylate, MW = 214, f = 2



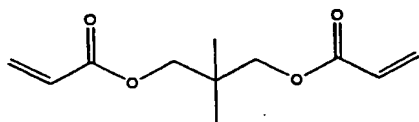
Ethoxylated Bisphenol A Diacrylate, MW = 424, f = 2

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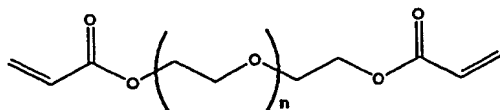
1,6-Hexanediol Diacrylate, MW = 226, f = 2

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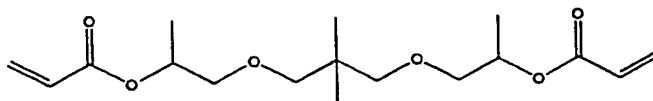
Neopentyl Glycol Diacrylate, MW = 212, f = 2

15



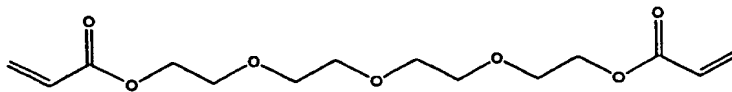
Polyethylene Glycol Diacrylate, MW = 302, 508, f = 2

20



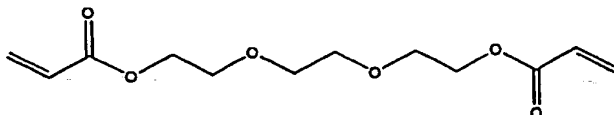
Propoxylated Neopentyl Glycol Diacrylate, MW = 328, f = 2

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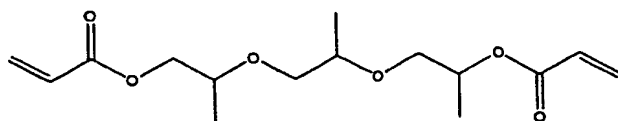


Tetraethylene Glycol Diacrylate, MW = 302, f = 2

30



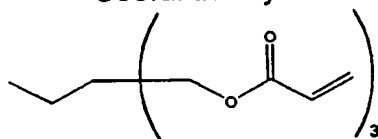
Triethylene Glycol Diacrylate, MW = 258, f = 2



Tripropylene Glycol Diacrylate (TRPGDA), MW = 300, f = 2

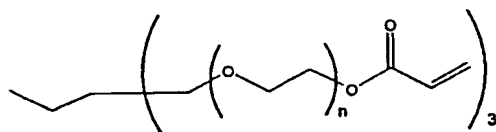
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Useful triacrylates are:

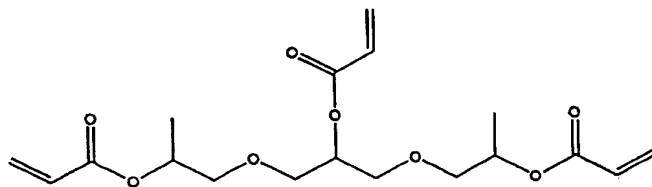


Trimethylolpropane Triacrylate (TMPTA), MW = 296, f = 3

10

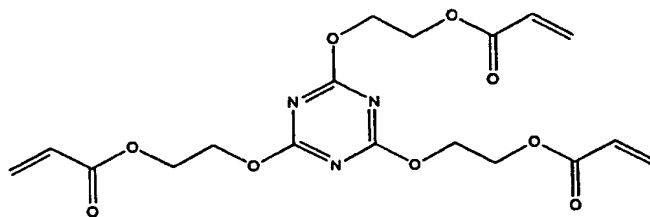
Ethoxylated Trimethylolpropane Triacrylate, MW =  $\geq 428$ , f = 3

15



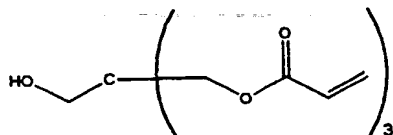
Propoxylated Glyceryl Triacrylate, MW = 428, f = 3

20

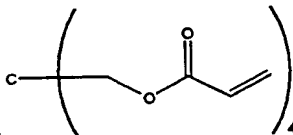


Tris (2-Hydroxy Ethyl) Isocyanurate Triacrylate, MW = 423, f = 3

25

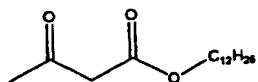
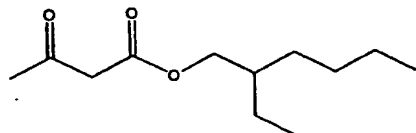
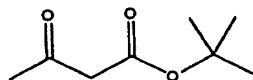
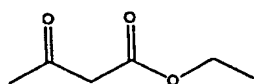
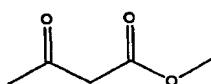


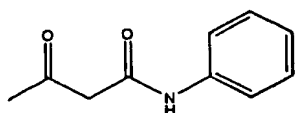
**Pentaerythritol Triacrylate, MW = 298, f = 3**



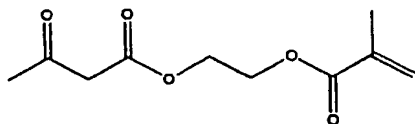
**5 Pentaerythritol Tetraacrylate (PETA), MW = 352, f = 4**

Useful acetoacetates having a functionality of two are:

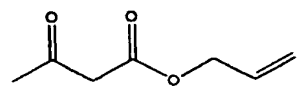


Acetoacetanilide,  $f = 2$ 

5

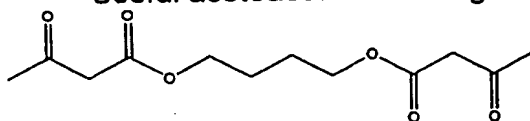
2-Acetoacetoxyethyl Methacrylate (AAEM),  $f = 2$ 

10

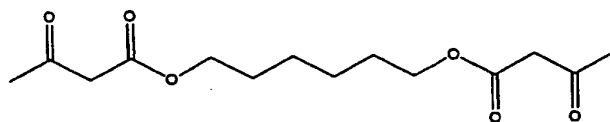
Allyl Acetoacetate,  $f = 2$ 

Useful acetoacetates having a functionality of four are:

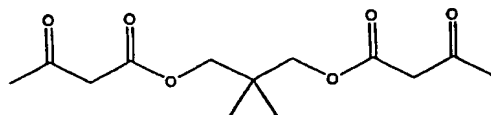
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Butanediol Diacetoacetate,  $f = 4$ 

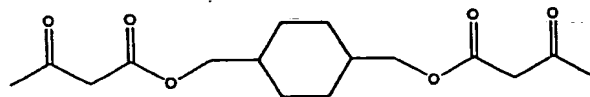
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1,6-Hexanediol Diacetoacetate,  $f = 4$ 

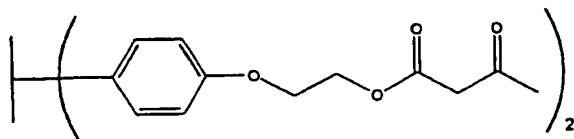
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Neopentyl Glycol Diacetoacetate,  $f = 4$ 

30

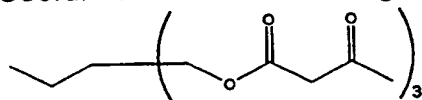
Cyclohexanedimethanol Diacetoacetate,  $f = 4$



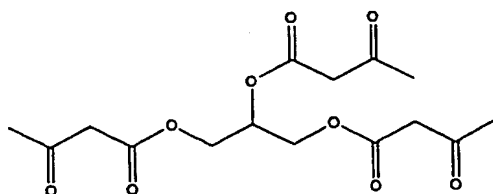


- 5 Ethoxylated Bisphenol A Diacetoacetate,  $f = 4$

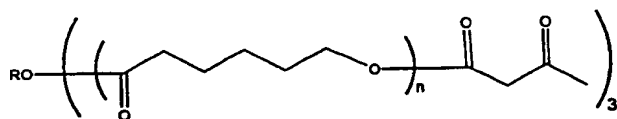
Useful acetoacetates having a functionality of six are:



- 10 Trimethylolpropane Triacetoacetate,  $f = 6$

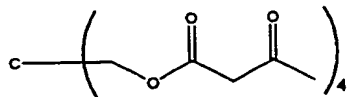


- 15 Glycerin triacetoacetate,  $f = 6$



- 20 Polycaprolactone triacetoacetate,  $f = 6$

A useful acetoacetate having a functionality of eight is:



- 25 Pentaerythritol Tetraacetoacetate,  $f = 8$

The Michael addition reaction is catalyzed by a strong base;  
diazabicycloundecene (DBU) is sufficiently strong and readily soluble in the

monomer mixtures. Other cyclic amidines, for example diazabicyclo-nonene (DBN) and guanidines are also suitable for catalyzing this polymerization.

Michael addition of a methacrylate functional  $\beta$ -dicarbonyl compound, 2-acetoacetoxyethyl methacrylate (AAEM), to diacrylate monomer yields  
5 liquid linear polyesters with reactive pendant methacrylate groups, which can be crosslinked in a subsequent curing reaction. As the acrylate and acetoacetate are mutually reactive and the methacrylate is inert under the conditions of the Michael addition, a highly functionalized (one methacrylate per repeat unit), liquid uncrosslinked polymer can be obtained in a one-step,  
10 ambient temperature, solventless reaction. The high selectivity of the Michael reaction permits the use of monomers such as styrene and methyl methacrylate as inert solvents to give low-viscosity systems that are easily incorporated into a variety of laminating resins.

In the following Examples all parts are by weight unless otherwise  
15 indicated. In addition, all references mentioned herein are specifically incorporated by reference.

A series of experiments defined the proportions of multi-acrylate to  $\beta$ -dicarbonyl acetoacetate which separate the liquid oligomer products of this invention from the gel or solid products of the prior art.

20

#### Synthetic Procedure:

An example of resin synthesis is as follows. Trimethylolpropane triacrylate (TMPTA) 59.2 g and diazabicycloundecene (DBU) 0.4 g were

weighed into a 500 ml 3-neck round bottom flask equipped with a mechanical stirrer and addition funnel. Ethyl acetoacetate (EAA) 13.0 g was weighed into the addition funnel. The TMPTA and DBU were mixed for 5 minutes prior to addition of the EAA. EAA was then added dropwise to the stirred

- 5 TMPTA/DBU mixture over a 15 minute period. The solution warmed after addition of EAA was complete. After the exotherm subsided a viscous yellow liquid was obtained which did not gel upon standing.

The same general procedure can be employed for a variety of combinations of acrylate and acetoacetate functional reactants, provided the equivalent ratio of acrylate : acetoacetate is sufficient to yield liquid, uncrosslinked products. For particularly exothermic or large scale reactions, controlled, gradual addition of acetoacetate and/or cooling of the reaction may be required to prevent premature, thermally initiated crosslinking of acrylate functional groups.

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**Table 1**

**Acetoacetate/Acrylate Mixtures**

20

	aceto- acetate	acrylate	f ratio	mole ratio	equiv ratio	weight ratio	reaction product
A	ethyl	hexanedi ol	2 : 2	1 : 1	2 : 2	36.5 : 63.5	viscous liquid*
B	ethyl	penta- erythritol	2 : 4	1 : 10	1 : 20	3.6 : 96.4	viscous liquid*
C	butanedi ol	hexanedi ol	4 : 2	1 : 1	2 : 1	53.3 : 46.7	crosslink ed gel**
D	penta- erythritol	penta- erythritol	8 : 4	1 : 10	1 : 5	11.8 : 88.2	crosslink ed gel**

- \* soluble in methyl ethyl ketone (MEK) at room temperature.
- \*\* insoluble in refluxing methyl ethyl ketone.

A and B made useful oligomers of the inventor. C and D made crosslinked gels which are outside the invention.

5

**Table 2**

Reactions of diacrylate acceptor with acetoacetate-functional donors.

Acceptor	Donor	Functionality ratio	Mole ratio	Equivalent ratio	Weight ratio	Reaction product
TRPGDA	MeOAcAc	2 : 2	1 : 1	1 : 1	72.1 : 27.9	sol
TRPGDA	EtOAcAc	2 : 2	1 : 1	1 : 1	69.8 : 30.2	sol
TRPGDA	aceto-acetanilide	2 : 2	1 : 1	1 : 1	62.9 : 37.1	sol
TRPGDA	butanedio l di-OAcAc	2 : 4	7.7 : 1	3.9 : 1	90 : 10	sol
TRPGDA		2 : 4	4.9 : 1	2.4 : 1	85 : 15	gel
TRPGDA		2 : 4	3.44 : 1	1.7 : 1	80 : 20	gel
TRPGDA	cyclohexane dimethanol di-	2 : 4	19.8 : 1	9.9 : 1	95 : 05	sol
TRPGDA	di-OAcAc	2 : 4	13.8 : 1	6.9 : 1	93 : 7	sol
TRPGDA		2 : 4	9.4 : 1	4.7 : 1	90 : 10	gel
TRPGDA		2 : 4	5.9 : 1	2.95 : 1	85 : 15	gel
TRPGDA		2 : 4	4.2 : 1	2.1 : 1	80 : 20	gel
TRPGDA	neopentyl glycol	2 : 4	8.2 : 1	4.1 : 1	90 : 10	sol
TRPGDA	di-OAcAc	2 : 4	5.1 : 1	2.6 : 1	85 : 15	sol
TRPGDA		2 : 4	3.6 : 1	1.8 : 1	80 : 20	gel
TRPGDA	TONE	2 : 6	16.6	5.5 : 1	90 : 10	sol

	0301 tri-OAcAc		: 1			
TRPGDA		2 : 6	10.4 : 1	3.5 : 1	85 : 15	gel
TRPGDA		2 : 6	7.4 : 1	2.5 : 1	80 : 20	gel
TRPGDA	glycerin tri-OAcAc	2 : 6	10.3 : 1	3.4 : 1	90 : 10	sol
TRPGDA		2 : 6	6.5 : 1	2.2 : 1	85 : 15	gel
TRPGDA		2 : 6	4.6 : 1	1.5 : 1	80 : 20	gel
TRPGDA	pentaeryt hritol tetra-OAcAc	2 : 8	14.2 : 1	3.5 : 1	90 : 10	sol
TRPGDA		2 : 8	8.9 : 1	2.2 : 1	85 : 15	gel
TRPGDA		2 : 8	6.3 : 1	1.6 : 1	80 : 20	gel

Review of Table 2 shows that certain diacrylate-acetoacetate equivalent ratios make sol or liquid oligomers of the invention.

**Table 3**

5

Reactions of triacrylate acceptor with acetoacetate-functional donors.

Accept or	Donor	Functionality ratio	Mole ratio	Equivalent ratio	Weight ratio	Reaction product
TMPTA	EtOAcAc	3 : 2	2 : 1	3 : 1	82 : 18	sol
TMPTA	EtOAcAc	3 : 2	3 : 2	2.25 : 1	77.4 : 22.6	sol
TMPTA	EtOAcAc	3 : 2	4 : 3	2 : 1	75.2 : 24.8	gel
TMPTA	butanediol di-OAcAc	3 : 4	7.8 : 1	5.9 : 1	90 : 10	sol
TMPTA		3 : 4	4.9 : 1	3.7 : 1	85 : 15	gel
TMPTA		3 : 4	3.5 : 1	2.6 : 1	80 : 20	gel
TMPTA	cyclohexane dimethanol di-	3 : 4	9.5 : 1	7.1 : 1	90 : 10	sol
TMPTA	di-OAcAc	3 : 4	6.0 : 1	4.5 : 1	85 : 15	gel
TMPTA		3 : 4	4.2 : 1	3.2 : 1	80 : 20	gel
TMPTA	neopentyl glycol	3 : 4	8.3 : 1	6.2 : 1	90 : 10	sol
TMPTA	di-OAcAc	3 : 4	5.2 : 1	3.9 : 1	85 : 15	gel

TMPTA		3 : 4	3.7 : 1	2.8 : 1	80 : 20	gel
TMPTA	TONE 0301 tri- OAcAc	3 : 6	16.8 : 1	8.4 : 1	90 : 10	sol
TMPTA		3 : 6	10.6 : 1	5.3 : 1	85 : 15	gel
TMPTA	glycerin tri-OAcAc	3 : 6	14.3 : 1	7.2 : 1	92.5 : 7.5	sol
TMPTA		3 : 6	10.5 : 1	5.2 : 1	90 : 10	gel
TMPTA	pentaeryt hritol tetra- OAcAc	3 : 8	30.3 : 1	11.4 : 1	95 : 5	sol
TMPTA		3 : 8	19.7 : 1	7.4 : 1	92.5 : 7.5	sol
TMPTA		3 : 8	14.4 : 1	5.4 : 1	90 : 10	gel

Review of Table 3 shows that certain triacrylate: acetoacetate ratios make sol or liquid oligomers of the invention.

**Table 4**

Reactions of tetraacrylate acceptor with acetoacetate-functional donors.

Accept or	Donor	Functionality ratio	Mole ratio	Equivalent ratio	Weight ratio	Reaction product
PETA	EtOAcAc	4 : 2	3.3 : 1	6.6 : 1	90 : 10	sol
PETA	EtOAcAc	4 : 2	2 : 1	4.0 : 1	84.4 : 15.6	gel
PETA	EtOAcAc	4 : 2	1 : 1	2 : 1	73 : 27	gel
PETA	butanediol di-OAcAc	4 : 4	13.9 : 1	13.9 : 1	95 : 5	sol
PETA		4 : 4	9.7 : 1	9.7 : 1	93 : 7	sol
PETA		4 : 4	6.6 : 1	6.6 : 1	90 : 10	gel
PETA	cyclohexane dimethanol di-OAcAc	4 : 4	16.8 : 1	16.8 : 1	95 : 5	sol
PETA	di-OAcAc	4 : 4	8.0 : 1	8 : 1	90 : 10	gel
PETA	neopentyl glycol	4 : 4	14.7 : 1	14.7 : 1	95 : 5	sol
PETA	di-OAcAc	4 : 4	10.3 : 1	10.3 : 1	93 : 7	sol
PETA		4 : 4	7.0 : 1	7 : 1	90 : 10	gel
PETA	TONE 0301 tri-OAcAc	4 : 6	29.8 : 1	19.9 : 1	95 : 5	sol
PETA		4 : 6	20.8 : 1	13.9 : 1	93 : 7	sol
PETA		4 : 6	14.1 : 1	9.4 : 1	90 : 10	gel
PETA	glycerin tri-OAcAc	4 : 6	18.6 : 1	12.4 : 1	95 : 5	sol
PETA		4 : 6	12.1 : 1	8 : 1	92.5 : 7.5	gel
PETA	pentaerythritol tetra-OAcAc	4 : 8	65.7 : 1	32.9 : 1	98 : 2	sol
PETA		4 : 8	43.3 : 1	21.7 : 1	97 : 3	sol
PETA		4 : 8	32.2 : 1	16.1 : 1	96 : 4	sol

			1			
PETA		4 : 8	25.5 : 1	12.7 : 1	95 : 5	sol
PETA		4 : 8	17.8 : 1	8.9 : 1	93 : 7	gel
PETA		4 : 8	12.1 : 1	6 : 1	90 : 10	gel

Review of Table 4 shows that certain tetracrylate:acetoacetate ratios make sol or liquid oligomers of the invention.

In order to demonstrate ultraviolet light crosslinking of these liquid oligomers, samples containing 1% (wt) Irgacure 500 photoinitiator and 0% photoinitiator  
5 were applied to release liner and spread to a thickness of 1.5 mil. Specimens were cured on a Fusion Systems Corp. uv curing unit, using an H-bulb and belt speed of 20-25 feet/minute; all formed transparent, flexible, nearly colorless films. Samples of each film were weighed, immersed in acetone (a  
10 good solvent for the uncured resins) at room temperature for 48 hours, blotted dry and re-weighed to determine solvent uptake. Specimens were then dried to constant weight in a vacuum oven at 80°C to determine gel fractions; these values are listed in the table 5 below.



**Table 5**

Solvent Uptake and Gel Fractions of UV Cured Methacrylate Functional Polyesters.

5

DIACRYLATE	Solvent Uptake, % (Irgacure 500, 1%)	Gel Fraction (Irgacure 500, 1%)	Solvent Uptake, % (No Photoinitiator)	Gel Fraction (No Photoinitiator)
NPG	18	94%	9	96%
PEG 200	19	96%	18	94%
Hexanediol	12	96%	9	96%
Triethylene glycol	16	95%	19	96%

These results confirm that the products are crosslinked and indicate no significant difference between products cured with or without added photoinitiator. This suggests that the pendant methyl ketone substituents serve as an internal or "built in" photoinitiator. To further demonstrate the role of methyl ketone substituents in the uv cure of these resins, three acrylate terminal resins were prepared from neopentyl glycol diacrylate and various  $\beta$ -dicarbonyl compounds in a 5:4 molar ratio.  $\beta$ -dicarbonyl compounds included acetylacetone (2 methyl ketones per molecule), ethyl acetoacetate (1 ketone/molecule) and diethyl malonate (no ketones). UV cure was performed as before, without added photoinitiator. Resins containing acetylacetone or ethyl acetoacetate cured to soft, tacky films. Such films are useful in

15

protective or decorative coatings on wood, or metal substrates. The resin containing diethyl malonate failed to cure, remaining liquid.

**Table 6**

**Reactions of Various Acrylate Acceptors and Michael Donors Having  
Functionality of Two**

	Acceptor Product	Donor	Equivalent Ratio	Oligomer
10	TRPGDA	ethyl acetoacetate	1:1	sol
		dimethyl malonate	1:1	sol
	f=2	ethyl cyanoacetate	1:1	sol
		acetoacetanilide	1:1	sol
		pentanedione	1:1	sol
15	TMPTA	ethyl acetoacetate	2.25:1	sol
		dimethyl malonate	2.5:1	sol
	f=3	ethyl cyanoacetate	2.5:1	sol
		acetoacetacetanilide	2.25:1	sol
20		pentanedione	3:1	sol
	PETA	ethyl acetoacetate	6.6:1	sol
		dimethyl malonate	4:1	sol
	f=4	ethyl cyanoacetate	5:1	sol
25		acetoacetanilide	4:1	sol
		pentanedione	3:1	sol

Review of Table 6 results reveals various Michael donors having 2 active  
hydrogens are useful, when reacted with acrylate acceptors, in making liquid  
oligomers.

We claim

1. A liquid oligomeric composition shelf stable for more than one month having residual pendant unsaturated acrylate groups, useful as a coating
- 5 when further polymerized comprising the organic soluble ungelled uncrosslinked Michael addition reaction product of:
- a) excess diacrylate acceptor, triacrylate acceptor, or tetraacrylate acceptor, and
- 10 b) an acetoacetate donor, having equivalent ratios of
- i) diacrylate acceptor :acetoacetate donor of
- 15  $\geq 1:1$  where acetoacetate functionality =2
- $\geq 4.5:1$  where acetoacetate functionality = 4
- $\geq 4.5:1$  where acetoacetate functionality = 6,
- 20  $\geq 3.5:1$  where acetoacetate functionality = 8,
- ii) triacrylate acceptor: acetoacetate donor of
- 25  $\geq 2.25$  where acetoacetate functionality =2
- $\geq 6.4:1$  where acetoacetate functionality = 4,
- $\geq 7.8:1$  where acetoacetate functionality = 6,
- 30  $\geq 7.4:1$  where acetoacetate functionality = 8,

iii) tetraacrylate acceptor: acetoacetate donor of

$\geq 6.6$  where acetacetate functionality = 2

5

$\geq 12.3:1$  where acetoacetate functionality = 4

$\geq 13.2:1$  where acetoacetate functionality = 6

10

$\geq 12.7 :1$  where acetoacetate functionality = 8.

2. The composition of Claim 1 wherein said reaction is carried out in the presence of a strong base.

15 3. The composition of Claim 1 wherein said diacrylate is  
diethylene glycol diacrylate,  
ethoxylated bisphenol A diacrylate,  
1,6-hexanediol diacrylate,  
neopentyl glycol diacrylate,  
20 polyethylene glycol (Mn 200) diacrylate,  
polyethylene glycol (Mn 400) diacrylate,  
propoxylated neopenyl glycol diacrylate,  
tetraethylene glycol diacrylate,  
triethylene glycol diacrylate, or  
25 tripropylene glycol diacrylate.

4. The composition of claim 1 wherein said tricrylate is:  
trimethylol propane triacrylate,  
ethoxylated trimethylolpropane triacrylate,  
30 tris (2-hydroxyethyl) isocyanurate triacrylate,

propoxylated glycerol triacrylate, or  
pentaerythritol triacrylate.

5     5.     The composition of Claim 1 wherein said tetraacrylate is  
pentaerythritol tetraacrylate.

6.     The composition of claim 1 wherein acetoacetates having 2 reactive  
functional groups per molecule are  
ethyl acetoacetate  
10    t-butylacetoacetate,  
methyl acetoacetate,  
2-ethylhexyl acetoacetate,  
lauryl acetoacetate,  
acetoacetanilide,  
15    2-acetacetoxoylethyl methacrylate, or  
allyl acetoacetate.

7.     The composition of claim 1 wherein acetoacetates having 4 functional  
groups per molecule are  
20    1,4 - butanediol diacetoacetate,  
1,6 - hexanediol diacetoacetate,  
neopentyl glycol diacetoacetate,  
cyclohexane dimethanol diacetoacetate, or  
ethoxylated bisphenol A diacetoacetate.

25

8.     The composition of Claim 1 wherein acetoacetates having 6 functional  
groups per molecule are  
trimethylol propane triacetoacetate,  
glycerin triacetoacetate, or  
30    polycaprolactone triacetoacetate.

9. The composition of claim 1 wherein said acetoacetate having 8 functional groups per molecule is pentaerythritol tetraacetate.
- 5 10. The composition of claim 2 wherein said base is diazabicycloundecene (DBU).
11. The composition of claim 1 wherein said reaction between a Michael donor acetoacetate and a Michael acceptor acrylate occurs in the presence  
10 of non-reactive solvents.
12. The composition of claim 11 wherein said solvent is styrene, t-butyl styrene, alpha methyl styrene, vinyl toluene, vinyl acetate, allyl acetate, allyl methacrylate, diallyl phthalate, C1 - C 18 methacrylate esters,  
15 dimethacrylates, or trimethacrylates.
13. The composition of Claim 12 further crosslinked in the presence of a free radical generating catalyst.
- 20 14. The composition of Claim 13 further comprising a photoinitiator.
15. A method of making a liquid oligomeric composition, stable for more than one month, having residual pendant unsaturated acrylate groups, useful as a coating when further polymerized in the absence of added  
25 photoinitiator, comprising the steps of reacting an acetoacetate donor having two, four, six, or eight reactive functional groups per molecule provided by acetoacetate groups and an excess of acrylate acceptor selected from the group of diacrylate, triacrylate, and tetra-acrylate in the presence of a strong base wherein the reactive equivalent functional ratios are:

30

a) diacrylate : acetoacetate of

$\geq 1:1$  where acetoacetate functionality = 2

5

$\geq 4.5:1$  where acetoacetate functionality = 4

$\geq 4.5:1$  where acetoacetate functionality = 6,

10

$\geq 3.5:1$  where acetoacetate functionality = 8,

b) triacrylate : acetoacetate of

$\geq 2.25$  where acetoacetate functionality = 2

15

$\geq 6.4:1$  where acetoacetate functionality = 4,

$\geq 7.8:1$  where acetoacetate functionality = 6,

20

$\geq 7.4:1$  where acetoacetate functionality = 8,

c) tetraacrylate : acetoacetate of

$\geq 6.6$  where acetoacetate functionality = 2

25

$\geq 12.3:1$  where acetoacetate functionality = 4

$\geq 13.2:1$  where acetoacetate functionality = 6

30

$\geq 12.7:1$  where acetoacetate functionality = 8,



wherein said diacrylate is selected from the group of  
diethylene glycol diacrylate,  
ethoxylated bisphenol A diacrylate,  
5 1,6-hexanediol diacrylate,  
neopentyl glycol diacrylate,  
polyethylene glycol (Mn200) diacrylate,  
polyethylene glycol (Mn400) diacrylate,  
propoxylated neopentyl glycol diacrylate,  
10 tetraethylene glycol diacrylate,  
triethylene glycol diacrylate,  
tripropylene glycol diacrylate, and

wherein said triacrylate is selected from the group of  
15 trimethylolpropane triacrylate,  
ethoxylated tromethylolpropane triacrylate,  
tris (2-hydroxyethyl) isocyanurate triacrylate,  
propoxylated glycerol triacrylate, and  
pentaerythritol triacrylate, and

20 wherein said tetraacrylate is pentaerythritol tetraacrylate.

16. The method of claim 15 wherein acetoacetates having 2 reactive  
25 functional equivalent groups per molecule provided by acetoacetate groups  
are  
ethyl acetoacetate,  
t-butylacetoacetate,  
methyl acetoacetate,  
30 2-ethylhexyl acetoacetate,

lauryl acetoacetate,  
acetoacetanilide,  
2-acetoacetoxyethyl methacrylate, or  
allyl acetoacetate.

5

17. The method of claim 15 wherein acetoacetates having 4 reactive functional equivalent groups per molecule provided by acetoacetate groups are

10 1,4- butanediol diacetoacetate  
1,6-hexanediol diacetoacetate,  
neopentyl glycol diacetoacetate,  
cyclohexane dimethanol diacetoacetate, or  
ethoxylated bisphenol A diacetoacetate.

15

18. The method of claim 15 wherein acetoacetates having 6 functional groups per molecule provided by acetoacetate groups are trimethylol propane triacetoacetate,

20 glycerin triacetoacetate, and  
polycaprolactone triacetoacetate.

19. The method of claim 15 wherein said acetoacetate having 8 functional group per molecule provided by acetoacetate groups is pentaerythritol

25 tetraacetoacetate.

20. The method of claim 15 wherein said strong base is diazabicycloundecene (DBU).

21. The method of Claim 15 wherein said reaction between a Michael donor acetoacetate and a Michael acceptor acrylate occurs in the presence of a solvent inert in the Michael reaction.
- 5 22. The method of Claim 15 wherein said solvent is styrene, t-butyl styrene, alpha methyl styrene, vinyl toluene, vinyl acetate, allyl acetate, allyl methacrylate, diallyl phthalate, C1 - C 18 methacrylate esters, dimethacrylates, or trimethacrylates.
- 10 23. The method of Claim 15 further crosslinked in the presence of a free radical generating catalyst.
24. The method of Claim 15 further comprising a photoinitiator.
- 15 25. A liquid oligomeric composition shelf stable for more than one month having residual pendant unsaturated acrylate groups, useful as a coating when further polymerized comprising the organic soluble ungelled uncrosslinked Michael addition reaction product of:
- 20 a) excess diacrylate acceptor, triacrylate acceptor, or tetraacrylate acceptor, and
- b) a Michael donor, having equivalent ratios of
- 25 I) diacrylate acceptor : Michael donor of
- $\geq 1:1$  where donor functionality = 2
- $\geq 4.5:1$  where donor functionality = 4

30

$\geq 4.5:1$  where donor functionality = 6,

$\geq 3.5:1$  where donor functionality = 8,

5           ii) triacrylate acceptor: Michael donor of

$\geq 2.25$  where donor functionality = 2

$\geq 6.4:1$  where donor functionality = 4,

10

$\geq 7.8:1$  where donor functionality = 6,

$\geq 7.4:1$  where donor functionality = 8,

15

iii) tetraacrylate acceptor: Michael donor of

$\geq 6.6$  where donor functionality = 2

$\geq 12.3:1$  where donor functionality = 4

20

$\geq 13.2:1$  where donor functionality = 6

$\geq 12.7 : 1$  where donor functionality = 8.

25   26. The composition of claim 25 wherein said donor is  
an acetoacetate,  
a malonic ester,  
pentanedione,  
acetoacetanilide  
30   o-acetoacetanisidide

*p*-acetoacetanisidide  
o-acetoacetotoluidide  
acetoacetamide  
N,N-dimethyl acetoacetamide

5

ethyl cyanoacetate  
methyl cyanoacetate  
butyl cyanoacetate  
octyl cyanoacetate, or  
10 cyanoacetamide

27. A method of making a liquid oligomeric composition, stable for more than one month, having residual pendant unsaturated acrylate groups, useful as a coating when further polymerized in the absence of added  
15 photoinitiator, comprising the steps of reacting a Michael donor having two, four, six, or eight reactive functional groups per molecule and an excess of acrylate acceptor selected from the group of diacrylate, triacrylate, and tetra-acrylate in the presence of a strong base wherein the reactive equivalent functional ratios are:

20

a) diacrylate : Michael donor of

$\geq 1:1$  where donor functionality = 2  
 $\geq 4.5:1$  where donor functionality = 4  
25  $\geq 4.5:1$  where donor functionality = 6,  
 $\geq 3.5:1$  where donor functionality = 8,

b) triacrylate : Michael donor of  
 $\geq 2.25$  where donor functionality = 2  
30  $\geq 6.4:1$  where donor functionality = 4,

$\geq 7.8:1$  where donor functionality = 6,

$\geq 7.4:1$  where donor functionality = 8,

c) tetraacrylate : Michael donor of

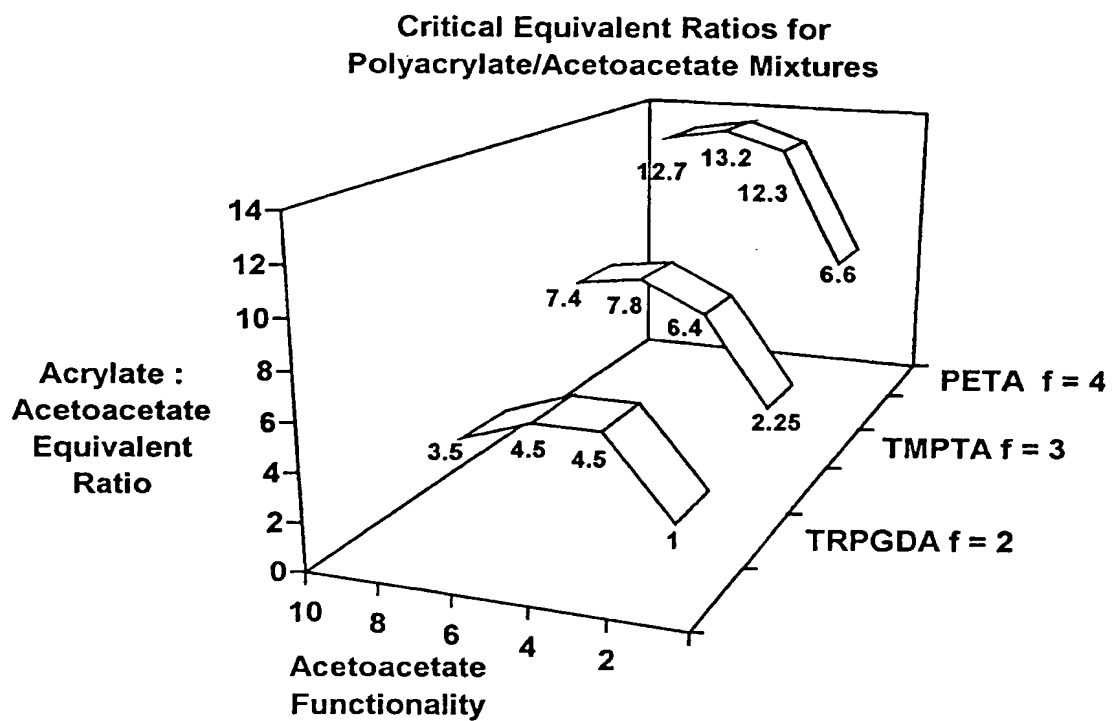
- 5  $\geq 6.6$  where donor functionality = 2  
 $\geq 12.3:1$  where donor functionality = 4  
 $\geq 13.2:1$  where donor functionality = 6  
 $\geq 12.7:1$  where donor functionality = 8,

- 10 wherein said diacrylate is selected from the group of  
diethylene glycol diacrylate,  
ethoxylated bisphenol A diacrylate,  
1,6-hexanediol diacrylate,  
neopentyl glycol diacrylate,  
15 polyethylene glycol (Mn200) diacrylate,  
polyethylene glycol (Mn400) diacrylate,  
propoxylated neopentyl glycol diacrylate,  
tetraethylene glycol diacrylate,  
triethylene glycol diacrylate,  
20 tripropylene glycol diacrylate, and

- wherein said triacrylate is selected from the group of  
trimethylolpropane triacrylate,  
ethoxylated trimethylolpropane triacrylate,  
25 tris (2-hydroxyethyl) isocyanurate triacrylate,  
propoxylated glycerol triacrylate, and  
pentaerythritol triacrylate, and

- wherein said tetraacrylate is pentaerythritol tetraacrylate.  
30

28. The method of Claim 27 wherein said donor having a functionality of 2 is selected from the group of acetoacetates,
- pentanedione,
- acetoacetanilide
- 5 *o*-acetoacetanisidide
- p*-acetoacetanisidide
- o*-acetoacetotoluidide
- acetoacetamide
- N,N-dimethyl acetoacetamide
- 10 ethyl cyanoacetate
- methyl cyanoacetate
- butyl cyanoacetate
- octyl cyanoacetate, and
- 15 cyanoacetamide





# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/14624

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) :C08F 2/50, 22/10, 122/10; C08G 2/02, 2/16. US CL :522/34, 36, 178, 182, 183; 526/ 321, 323.1, 232.2, 325; 528/220. According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 522/34, 36, 178, 182, 183; 526/ 321, 323.1, 232.2, 325; 528/220. Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS: acetoacetate, di-, tri- tetra-acrylate, Michael addition, Micael acceptor, Michael donor		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 580 328 A2 (ROHM AND HAAS CO.) 26 January 1994, see the Abstract, page 2, lines 12-28.	1-28
Y	US 5,459,178 A (CHAN et al) 17 October 1995, Abstract, Examples and Table II.	1-28
Y	US 5,539,017 A (RHEINBERGER et al) 23 July 1996, column 2, lines 18-58, and column 4, lines 11-19.	1-28
Y	RECTOR, F. DEL et al, "Applications for Acetoacetyl Chemistry in Thermoset Coatings", Journal of Coatings Technology, Vol. 61, No. 771, April 1989.	1-28
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *&* document member of the same patent family	
Date of the actual completion of the international search 01 OCTOBER 1999		Date of mailing of the international search report 21 OCT 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer SUSAN BERMAN Telephone No. (703) 308-0651